Sintering characteristics of nano-ceramic coatings

Popma, Ronald Leo Wim

1. INTRODUCTION

The origin of the word ceramic stems from the Greek *κεραμικος,* from *κεραμος* potter's clay, pottery. A century ago there were three sorts of ceramics: earthenware, stoneware and porcelain. Earthenware is a colored mass that is porous (absorbs liquid) before it is glazed. It is fired at a temperature around 1000 °C. Stoneware is a hard material fired in high temperature kilns generally around 1200 °C to 1400 °C. At this temperature, stoneware vitrifies (becomes glass-like); the resulting product is less than 2% porous. Finally porcelain is made of Kaolin (white clay) and Pentuntse (pulverized granite). When fired at a temperature of 1300 °C to 1400 °C these ingredients produce a white, more or less translucent, glass-like material. These examples clearly illustrate some of the characteristics of the sintering process. To produce strength in the shaped powder a certain heat treatment is required. Sintering temperatures are usually around half of the absolute melting temperature of the material. Sintering lowers the surface energy by reducing the surface area. Many properties including strength, ductility, conductivity, magnetic permeability and corrosion resistance are dramatically improved during sintering. To understand the evolution of various properties requires a study of the development of the microstructure.

Nowadays ceramic coatings are widely used for their superb performance in applications where metals may fail. In particular, applications are sought in circumstances where materials have to withstand high temperatures, corrosive environments and severe wear. Besides coatings, complex millimeter-sized 3D-ceramic/metal products are of interest. Major problems in this area include the large number of costly process steps, the high percentage of wasted material and a rather unpredictable shrinkage during sintering. The conventional method of slip casting to produce ceramic foils suffers to a certain extent from thickness limitations. An industrially applicable method to obtain coatings is wet-chemical processing, also called sol-gel processing. Indeed, sol-gel coatings can be used in many more applications than for protection only, such as in the optical and electronic industries. From a technical viewpoint wet-chemical processing offers many advantages. The sol-gel method allows films to be made with almost any composition and degree of porosity. The problem of homogeneity, often encountered in the processing of powders, is fully absent in the sol-gel preparation technique because no comminution is required. Moreover the processing temperatures can be significantly reduced, and combining different coating liquids (hybrid systems) is easy. This latter aspect offers a great deal of freedom to fabricate coatings with different properties. Finally the introduction of organic or conductive additives into the product is possible.

1.1. PROBLEM DEFINITION

The work described in this thesis is part of an international collaboration between our department of applied physics and Philips, Fraunhofer, Merck, Pelikan, Sandvik and Xaarjet (MIT). The project has been named ACERLINK, which stands for Additive mass manufacturing of composite CERamic, metal and glass microparts and multilayers from nano-sized particles using Laser and INK-jet technology. The basic idea is to combine the sol-gel concept with inkjet technology and laser treatment of surfaces[1]. A solution containing nano-sized ceramic particles is fed to an inkjet nozzle that generates a software-controlled pattern on a surface. Afterwards the drops are exposed to an intense laser beam that gives rise to drying and densification of the drops, thereby forming a sintered ceramic layer. Our work concentrates on the morphology of the nanoceramic layers examined with advanced microscopy techniques to reveal the sintering mechanism. In the latter the thermo-physical properties are relevant for the in coupling of the laser beam. Quantitative predictions for the densification process are made based on a theoretical analysis.

Motivation for this fundamental work stems from a strategic technology viewpoint: industrial companies manufacturing complex millimeter-sized ceramic mass products, typically made from plates or bars containing many products suffer the problems of the complexity and inflexibility of the batch oriented processes. The separation of ceramic microparts causes up to 30 % waste of material. Ceramic products seriously deform during sintering. Ceramic foils cannot be made in layers below 5 μm thick while much thinner layers are needed. In the coating industry the usual CVD process for producing wear resistant layers is very time consuming and cannot be applied locally.

In the Acerlink project that is part of the EU-BRITE/EURAM program, a new technology has been proposed to offer product-design freedom in ceramics, glass and even metals. In principle also UV-curing plastic monomers could be processed using a UV laser (stereolithography with inkjet). The proposal suggests to print a sol of nanosized particles by inkjet technology, and to dry and laser sinter the printed ceramics using a single on-line system. Multiple process cycles ('stereostiction') may provide composite ceramic/metal/glass structures of arbitrary patterns (also 3-dimensional) without subsequent subtractive shaping, trimming or product separation. Due to the additive nature of the new technology and the flexibility of both inkjet and laser technologies the main benefits expected are:

Reduction of manufacturing costs by up to 5 times reduction of the number of processing steps; full software control allows mass production with batch size of 1 piece. Additive processes produce no waste material for product separation, giving up to 30 % reduction in material cost and environmental load. Minimum layer thickness 0.1 μm, nominally 0.1-0.5 μm per printing pass and printing speed required to be at least 0.0005 m^2/sec; the aim is 50 μm line width and 5 μm landing accuracy.

The first objective is 2-D local patterning of wear-resistant layers on various materials. The second objective is 2-D patterning and composite generation using the 'multicolor' capability of inkjet technology using colloidal sols of different materials made via the sol-gel route instead of colored inks. The third objective is 3-D shaping with ready sintered ceramics in multi-pass with a sliced CAD-design where patterns are stacked. The fourth objective is to reduce costs and environmental impact by the additive nature of the technology and by the use of water based matrices instead of organic solvents.

1.2. OUTLINE OF THIS THESIS

Chapter 2 discusses the main experimental tools that have been used for the sintering experiments. Ellipsometry, High Resolution Scanning Electron Microscopy, Transmission Electron Microscopy Digital Image Manipulation and nano-indentation techniques are described. The laser systems used are also presented.

In Chapter 3 the temperature models of the laser heat treatment of the sol-gel coatings are derived. The model develops from a steady state model towards a dynamic model with a multi-pass laser source and heat-treated ceramic material with temperature dependent material properties.

Chapter 4 concentrates on the sintering behavior of silica sol-gels. It starts with a description of different sintering models that are used to predict the viscous sintering process. Via an extensive experimental part it leads to a description of the influence of the colloid size and other sintering parameters such as temperature and time on the resulting mechanical properties of the created silica coatings.

Chapter 5 presents the crystalline sintering behavior of zirconia sol-gel coatings deposited on fused silica and steel. Experimental results of furnace and laser treatments show the densification behavior and the grain growth in the thin film.

In Chapter 6 the work is summarized and an outlook towards future research is presented based on the results from the previous chapters.

1.3. REFERENCES

1 J.T.M. De Hosson and D.H.J. Teeuw, in Lasers in Surface Science and Engineering; Vol. 1, edited by N. B. Dahotre (1998), p. 205-255.